339.7755USU

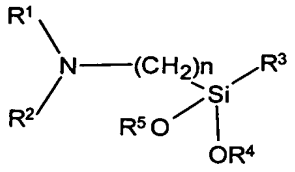
We claim:

1. A non-photosensitive polyimide precursor composition comprising:

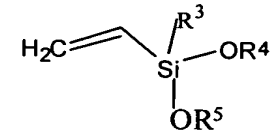
a) one or more polyamic acids soluble in *gamma*-butyrolactone (GBL) and aqueous tetramethyl ammonium hydroxide, , and with the proviso that the polyamic acid is also resistant to a solvent used in a photosensitive composition with which the polyimide precursor composition is to be used;

b) a solvent comprising *gamma*-butyrolactone; and

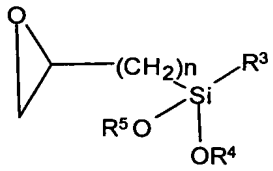
c) one or more adhesion promoters selected from the group consisting of the structures described by Formulae I-VI



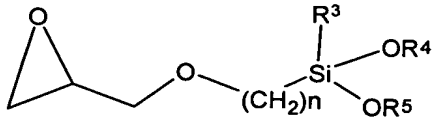
I



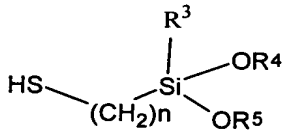
II



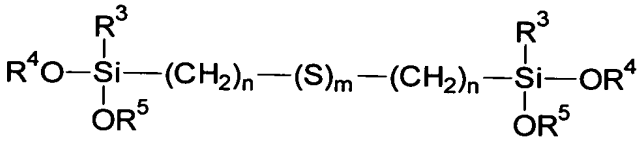
III



IV



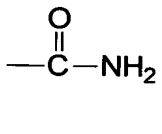
V



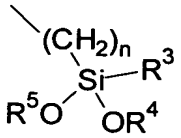
VI

wherein R^1 is selected from the group consisting of H, C_1 –C_{10} linear, cyclic or branched alkyl, phenyl, halophenyl and alkyl substituted phenyl, R^2 is selected from the group consisting of C_1 –C_{10} linear, cyclic or branched alkyl, phenyl, halophenyl

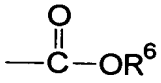
and alkyl substituted phenyl or one of the following moieties VII, VIII , or IX



VII



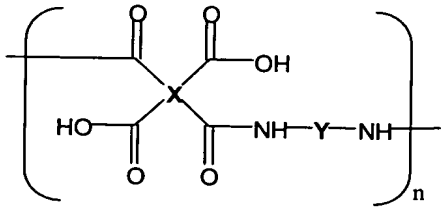
VIII



IX

where R^3 is C_1 –C_4 linear or branched alkyl or C_1 –C_4 linear or branched alkoxy group, R^4 , R^5 and R^6 are independently a C_1 –C_4 linear or branched alkyl group, m is an integer from 1 to about 4, and n is an integer from 1 to about 5.

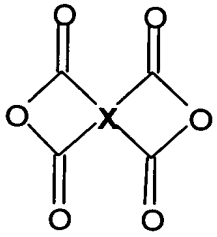
2. A composition according to claim 1 wherein the one or more polyamic acids is selected from the group consisting of polyamic acids of the Formula X



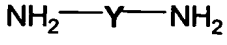
X

where n is an integer ranging from about 5 to about 200 wherein **X** and **Y** are independently selected from aromatic and aliphatic moieties which may contain heteroatoms.

3. A composition according to claim 2 wherein the one or more polyamic acids of Formula X is one prepared by reacting at least one anhydride monomer of Formula XI with at least one diamine monomer of Formula XII



XI



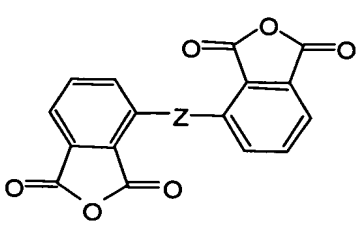
XII

and wherein the anhydride monomer is selected from the group consisting of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 3,3',4,4' diphenylsulfidetetracarboxylic acid dianhydride, 3,3'4,4'-diphenylsulfontetracarboxylic acid dianhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic acid dianhydride, 2,2',3,3' -diphenylmethanetetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,4,5,7-naphtnalenetetracarboxylic acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 1,3-diphenylhexafluoropropane-3,3,4,4-tetracarboxylic acid dianhydride, 1,4,5,6- naphthalenetetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic acid dianhydride, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 1,2,4,5 naphthalenetetracarboxylic acid dianhydride, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 1,8,9,10-phenanthrenetetracarboxylic acid dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, 1,2,3,4-benzenetetracarboxylic acid dianhydride and 1,2,4,5-benzenetetracarboxylic acid dianhydride, and the diamine monomer is selected from the group consisting of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane, *m*-phenylenediamine, *p*-phenylenediamine, 2,2'-bis(trifluoromethyl)-4,4'-diamino-1,1'-biphenyl, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 2,4-tolylenediamine,

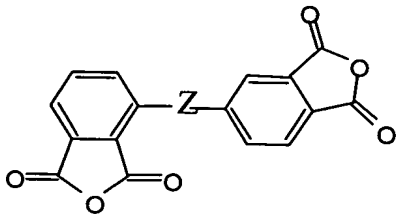
3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ketone, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 1,3-bis (4-aminophenoxy) benzene, 1,3-bis(3-amino-phenoxy) benzene, 1,4-bis (γ-aminopropyl)tetramethyldisiloxane, 2,3,5,6-tetramethyl-*p*-phenylenediamine, *m*-xylylenediamine, *p*-xylylenediamine, methylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, 2,5-dimethylhexamethylenediamine, 3-methoxyhexamethylenediamine, heptamethylenediamine, 2,5-dimethylheptamethylenediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, octamethylenediamine, nonamethylenediamine, 2,5-dimethylnonamethylenediamine, decamethylenediamine, ethylenediamine, propylenediamine, 2,2-dimethylpropylenediamine, 1,10-diamino-1,10-dimethyldecane, 2,11-diaminidodecane, 1,12-diaminooctadecane, 2,17-diaminoeicosane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, bis(4-aminocyclohexyl)methane, bis(3-aminonorbornyl)methane, 3,3'-diaminodiphenylethane, 4,4'-diaminodiphenylethane, and 4,4'-diaminodiphenyl sulfide, 2,6-diaminopyridine, 2,5-diaminopyridine, 2,6-diamino-4-trifluoromethylpyridine, 2,5-diamino-1,3,4,-oxadiazole, 1,4-diaminocyclohexane, piperazine, 4,4'-methylenedianiline, 4,4'-methylene-bis(o-choloroaniline), 4,4'-methylene-bis(3-methylaniline), 4,4'-methylene-bis(2-ethylaniline), 4,4'-methylene-bis(2-methoxyaniline), 4,4'-oxy-dianiline, 4,4'-oxy-bis-(2-methoxyaniline), 4,4'-oxy-bis-(2-chloroaniline), 4,4'-thio-dianiline, 4,4'-thio-bis-(2-methylaniline), 4,4'-thio-bis-(2-methyoxyaniline), 4,4'-thio-bis-(2-chloroaniline), 3,3'sulfonyl-dianiline, and 3,3'sulfonyl-dianiline.

4. A composition according to claim 3 wherein the anhydride monomer is

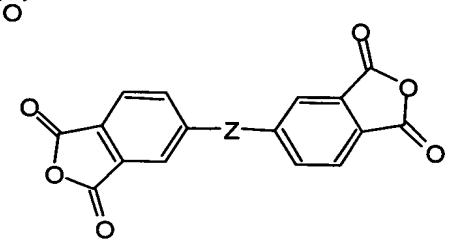
selected from the group consisting of a compound selected from the group consisting of compounds described by the structures (XIII - XV):



XIII



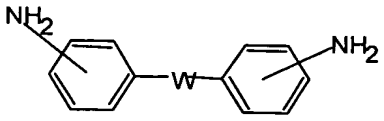
XIV



XV

where Z= is selected from the group consisting of -O-, -S-, -$C(CF_3)_2$-, -CH_2-, -SO_2-, -NHCO- or –$Si(R')_2$- where R' is a linear, branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

5. A composition according to claim 4 wherein the diamine monomer is at least one compound having the structure XVI



XVI

where W= is selected from the group consisting of -O-, -S-, -$C(CF_3)_2$-, -CH_2-, -SO_2-, -NHCO- and –$Si(R')_2$- where R' is a linear branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

6. A composition according to claim 5 wherein Z is –O- and W is –O-.

7. A composition according to claim 3 wherein the one or more polyamic acids is a polyamic acid selected from the group consisting of those from a polyamic acid from 4,4'-diaminodiphenyl ether and 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, a polyamic acid polymer from 4,4'-diaminodiphenyl ether and a mixture of 95-85% of 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride and 5-15% of another anhydride of Formula XI.

8. A composition according to claim 2 wherein the ratio of diamine to dianhydride units in the polyamic acid of Formula X is from about 0.9 to about 1.

9. A composition according to claim 1 wherein the % of polyamic acid in the composition is from about 6 to about 23 % by weight of the composition.

10. A composition according to claim 1 wherein the % of polyamic acid in the composition is from about 12 to about 22 % by weight of the composition.

11. A composition according to claim 10 wherein the solvent comprise from about 74% to about 92% by weight of the composition.

12. A composition according to claim 11 wherein the composition contains at

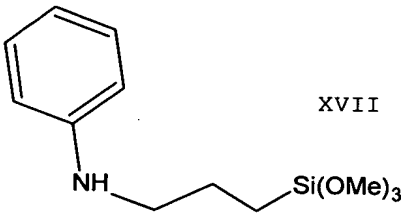
least one cosolvent having a boiling point of between about 110 °C and about 230 °C.

13. A composition according to claim 12 wherein the cosolvent is selected from the group consisting of *gamma*-valerolactone, *gamma*-caprolactone, *delta*-valerolactone, 2-hexanone, 3-hexanone, 2-heptanone, 3-heptanone, and 4-methyl -2-pentanone.

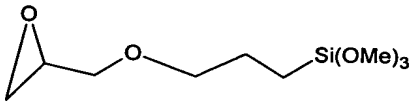
14. A composition according to claim 1 wherein the adhesion promoter is one selected from those of the Formulae I, II, IV and V.

15. A composition according to claim 1 wherein the adhesion promoter is one of Formula I wherein R^1 and R^2 are each independently C_1–C_{10} linear, cyclic or branched alkyl or one of R^1 and R^2 is phenyl.

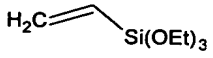
16. A composition according to claim 1 wherein the adhesion promoter is selected from the group consisting of those of Formulae XVII, XVIII, XIX, and XX



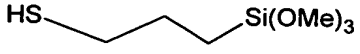
XVII



XVII



XIX



XX.

17. A composition according to claim 1 wherein the adhesion promoter comprises from about 0.05% to about 1.5% by weight of the composition.

18. A process for producing a patterned polyimide structure on a substrate, the process comprising the steps of:

(a) providing a substrate;

(b) in a first coating step, coating the substrate with a non-photosensitive polyimide precursor composition of claim 1;

(c) baking the layer of non-photosensitive polyimide precursor composition at a temperature or temperatures below 140 °C;

(d) in a second coating step, coating a layer of a photoresist over the layer of non-photosensitive polyimide precursor composition to form a bilayer coating;

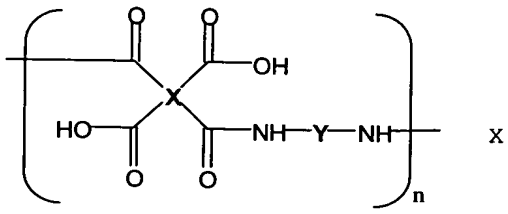
(e) exposing the bilayer coating to radiation suitable appropriate for the photoresist;

(f) developing the bilayer coatings with one or more aqueous developers;

(g) removing the remaining photoresist layer; and

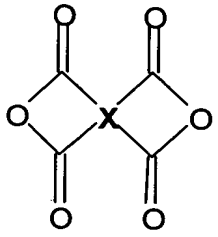
(h) curing the non-photosensitive polyimide precursor composition layer at a temperature at least about 200 °C to produce a polyimide structure.

19. A process according to claim 18 wherein the one or more polyamic acids in the non-photosensitive polyimide precursor composition is selected from the group consisting of polyamic acids of the Formula X

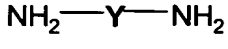


where n is an integer ranging from about 5 to about 200 wherein **X** and **Y** are independently selected from aromatic and aliphatic moieties which may contain heteroatoms.

20. A process according to claim 19 wherein the one or more polyamic acids of Formula X is one prepared by reacting at least one anhydride monomer of Formula XI with at least one diamine monomer of Formula XII



XI



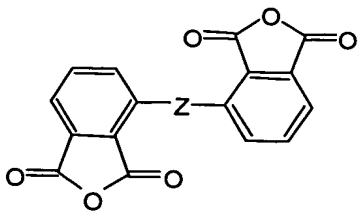
XII

and wherein the anhydride monomer is selected from the group consisting of 3,3',4,4'-biphenyltetracarboxylic acid dianhydride, 3,3',4,4' diphenylsulfidetetracarboxylic acid dianhydride, 3,3'4,4'-diphenylsulfontetracarboxylic acid dianhydride, 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride, 3,3',4,4'-diphenylmethanetetracarboxylic acid dianhydride, 2,2',3,3' -diphenylmethanetetracarboxylic acid dianhydride, 2,3,3',4'-biphenyltetracarboxylic acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,4,5,7-naphtnalenetetracarboxylic acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(2,3-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 1,3-diphenylhexafluoropropane-3,3,4,4-tetracarboxylic acid dianhydride, 1,4,5,6- naphthalenetetracarboxylic dianhydride, 2,2',3,3'-diphenyltetracarboxylic acid dianhydride, 3,4,9,10-perylenetetracarboxylic acid dianhydride, 1,2,4,5 naphthalenetetracarboxylic acid dianhydride, 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 1,8,9,10-phenanthrenetetracarboxylic acid dianhydride, 1,1-bis(2,3-dicarboxyphenyl)ethane dianhydride, 1,1-bis(3,4-dicarboxyphenyl)ethane dianhydride, 1,2,3,4-benzenetetracarboxylic acid dianhydride and 1,2,4,5-

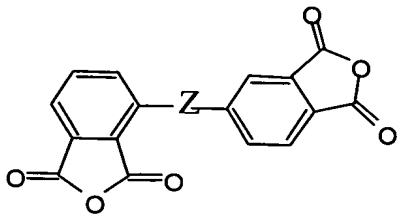
benzenetetracarboxylic acid dianhydride, and the diamine monomer is selected from the group consisting of 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane, *m*-phenylenediamine, *p*-phenylenediamine, 2,2'-bis(trifluoromethyl)-4,4'-diamino-1,1'-biphenyl, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 2,4-tolylenediamine, 3,3'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenylmethane, 3,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ketone, 3,3'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 1,3-bis (4-aminophenoxy) benzene, 1,3-bis(3-amino-phenoxy) benzene, 1,4-bis (γ-aminopropyl)tetramethyldisiloxane, 2,3,5,6-tetramethyl-*p*-phenylenediamine, *m*-xylylenediamine, *p*-xylylenediamine, methylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, 2,5-dimethylhexamethylenediamine, 3-methoxyhexamethylenediamine, heptamethylenediamine, 2,5-dimethylheptamethylenediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, octamethylenediamine, nonamethylenediamine, 2,5-dimethylnonamethylenediamine, decamethylenediamine, ethylenediamine, propylenediamine, 2,2-dimethylpropylenediamine, 1,10-diamino-1,10-dimethyldecane, 2,11-diaminidodecane, 1,12-diaminooctadecane, 2,17-diaminoeicosane, 3,3'-dimethyl-4,4'-diaminodiphenylmethane, bis(4-aminocyclohexyl)methane, bis(3-aminonorbornyl)methane, 3,3'-diaminodiphenylethane, 4,4'-diaminodiphenylethane, and 4,4'-diaminodiphenyl sulfide, 2,6-diaminopyridine, 2,5-diaminopyridine, 2,6-diamino-4-trifluoromethylpyridine, 2,5-diamino-1,3,4,-oxadiazole, 1,4-diaminocyclohexane, piperazine, 4,4'-methylenedianiline, 4,4'-methylene-bis(o-choloroaniline), 4,4'-methylene-bis(3-methylaniline), 4,4'-methylene-bis(2-ethylaniline), 4,4'-methylene-bis(2-methoxyaniline), 4,4'-oxy-dianiline, 4,4'-oxy-bis-(2-methoxyaniline), 4,4'-oxy-bis-(2-chloroaniline), 4,4'-thio-

dianiline, 4,4'-thio-bis-(2-methylaniline), 4,4'-thio-bis-(2-methyoxyaniline), 4,4'-thio-bis-(2-chloroaniline), 3,3'sulfonyl-dianiline, and 3,3'sulfonyl-dianiline.

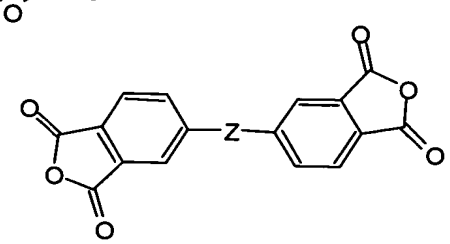
21. A process according to claim 20 wherein the anhydride monomer is selected from the group consisting of a compound selected from the group consisting of compounds described by the structures (XIII - XV):



XIII



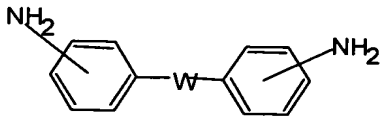
XIV



XV

where Z= is selected from the group consisting of -O-, -S-, -$C(CF_3)_2$-, -CH_2-, -SO_2-, -NHCO- or –$Si(R')_2$- where R' is a linear, branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

22. A process according to claim 21 wherein the diamine monomer is at least one compound having the structure XVI



XVI

where W= is selected from the group consisting of -O-, -S-, -$C(CF_3)_2$-, -CH_2-, -SO_2-, -NHCO- and –$Si(R')_2$- where R' is a linear branched or cyclic alkyl group containing from 1 to 8 carbon atoms.

23, A process according to claim 22 wherein Z is –O- and W is –O-.

24. A process according to claim 20 wherein the one or more polyamic acids is a polyamic acid selected from the group consisting of those from a polyamic acid from 4,4'-diaminodiphenyl ether and 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride, a polyamic acid polymer from 4,4'-diaminodiphenyl ether and a mixture of 95-85% of 3,3',4,4'-diphenyloxidetetracarboxylic acid dianhydride and 5-15% of another anhydride of Formula XI.

25. A process according to claim 19 wherein the ratio of diamine to dianhydride units in the polyamic acid of Formula X is from about 0.9 to about 1.

26. A process according to claim 18 wherein the % of polyamic acid in the composition is from about 6 to about 23 % by weight of the composition.

27. A process according to claim 18 wherein the % of polyamic acid in the composition is from about 12 to about 22 % by weight of the composition.

28. A process according to claim 27 wherein the solvent comprise from about 74% to about 92% by weight of the composition.

29. A process according to claim 28 wherein the composition contains at least one cosolvent having a boiling point of between about 110 °C and about 230

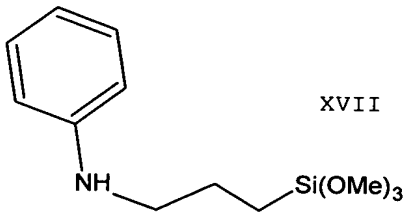
°C.

30. A process according to claim 29 wherein the cosolvent is selected from the group consisting of *gamma*-valerolactone, *gamma*-caprolactone, *delta*-valerolactone, 2-hexanone, 3-hexanone, 2-heptanone, 3-heptanone, and 4-methyl -2-pentanone.

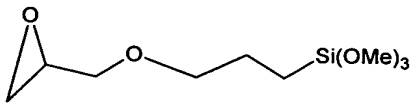
31. A process according to claim 18 wherein the adhesion promoter is one selected from those of the Formulae I, II, IV and V.

32. A process according to claim 18 wherein the adhesion promoter is one of Formula I wherein R^1 and R^2 are each independently C_1–C_{10} linear, cyclic or branched alkyl or one of R^1 and R^2 is phenyl.

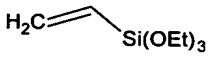
33. A process according to claim 18 wherein the adhesion promoter is selected from the group consisting of those of Formulae XVII, XVIII, XIX, and XX



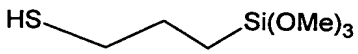
XVII



XVIII



XIX



XX.

34. A process according to claim 18 wherein the adhesion promoter comprises from about 0.05% to about 1.5% by weight of the composition.

35. A process according to claim 18 wherein in step c) the baking occurs at a temperature or temperatures below 130°.

36. A patterned polyimide structure on a substrate produced according to the

process of claim 18.